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Demonstration of Lithographic Patterning in Measurements of General and Localized Corrosion on Alloy 22

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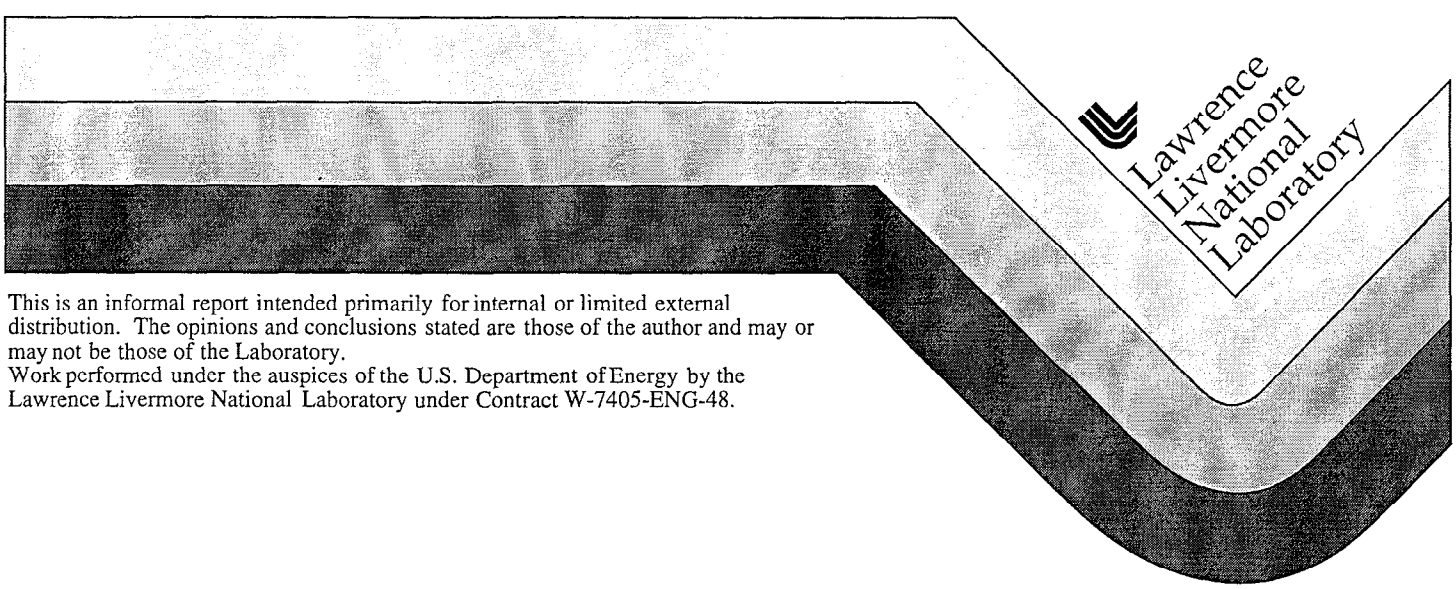
Joseph C. Farmer

July 1999



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Demonstration of Lithographic Patterning in Measurements of General and Localized Corrosion on Alloy 22

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Abstract

We have demonstrated a new technique capable of detecting generalized corrosion of metallographically-polished materials with nanometer-scale precision. After exposing a lithographically-patterned coupon of Alloy 22 to an electrolyte in a potentiostatically-controlled cell for twenty-four hours, we detected the loss of up to 130nm of metal In addition, "wormholes" were detected at certain points of intersection of three grain boundaries.

Introduction

The emphasis on the use of Corrosion-Resistant Materials (CRM's) in the Engineered Barrier Systems (EBS) for the proposed Geological Repository has stimulated the exploration of novel techniques for detecting corosion in trace amounts which may be undetectable by traditional methods such as weight loss. The Atomic Force Microscope (AFM), with its atomic-level sensitivity to surface topography, enables the detection of nanometer-scale changes in surface topography introduced by corrosion. The detection of the effects of aqueous corrosion on such a fine scale is made necessary by the need to predict over a geological time scale the performance of materials which typically do not corrode macroscopically over the time scale of laboratory tests in relevant environments.

The procedure used here is illustrated in Figure 1. A test coupon is first polished metallographically to a mirror finish with a total rms roughness below 2 nm, as measured with an AFM. Next, it is patterned with a series of photoresist lines. The masked sample is then exposed to an electrolyte in a potentiostatically-controlled cell for some fixed time. Once the sample is removed, the mask is dissolved away with acetone. After the removal of corrosion products and mineral deposits, what remains is a grating in which lines of protected base metal alternate with lines of exposed material. If the corrosion resulted in the dissolution of metal, then the lines of exposed material will be depressed. The amount of material lost can then be measured directly with an AFM.

The experiments described below are covered under the YMP Approved Activity Plan AP-E20-70. Sample preparation procedures are covered under the YMP Approved TIP AP-E20-71. Sample numbers refer to YMP controlled coupon designations. Image numbers are identical to the controlled file names.

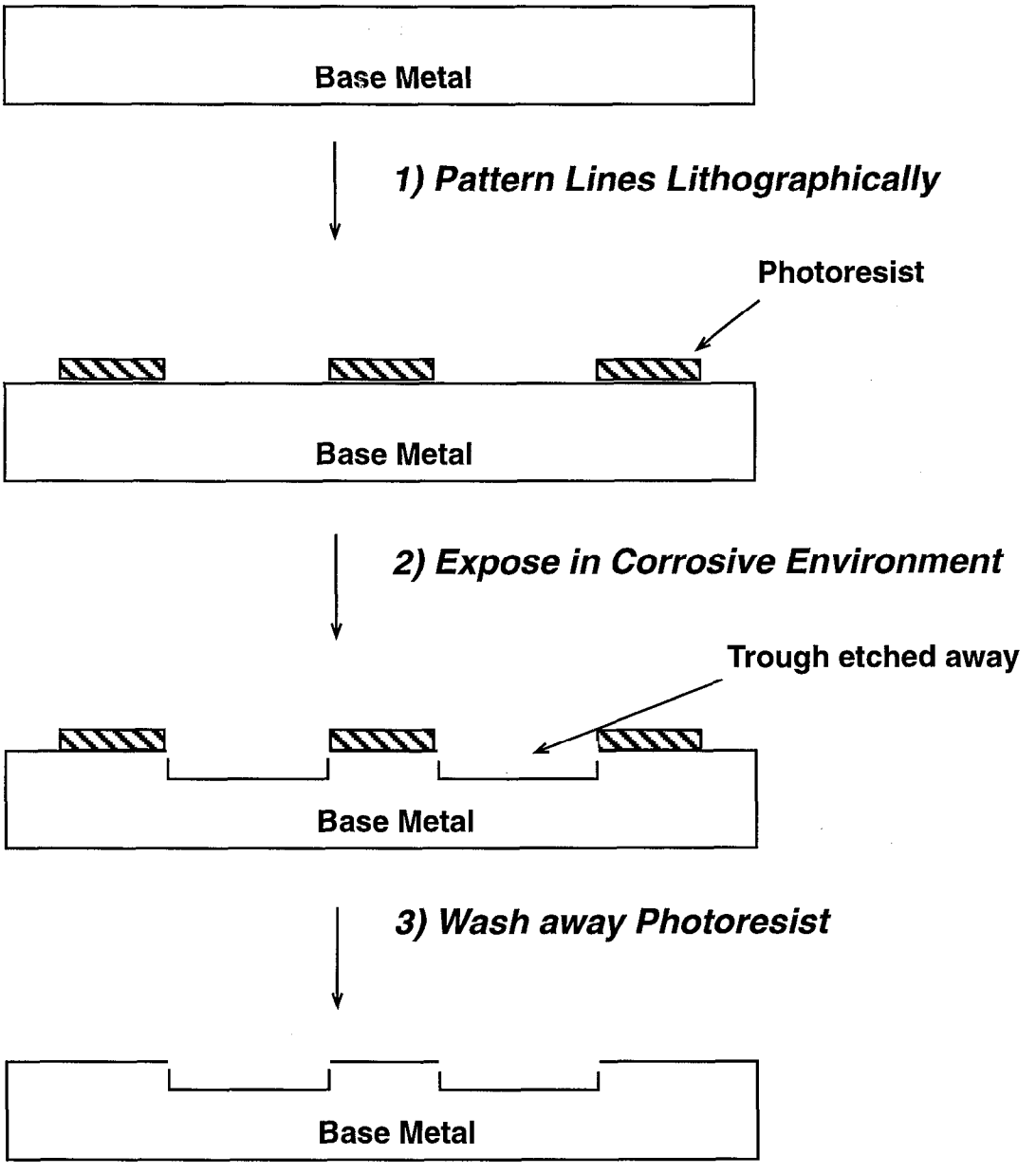

Figure 1: Method for AFM-based detection of metal dissolution by corrosion.

Method

Alloy 22 Test Coupon DEA325 was lithographically patterned with a photoresist mask and then exposed to Simulated Concentrated Well Water (SCW) at 90°C for 24 hours, at +200mV with respect to a Ag/AgCl reference electrode. Following the polarization, the mask was removed by repeated heating and ultrasonic agitation of the sample in Acetone. A scale buildup was removed by ultrasonic agitation in deionized water.

Observations

The observations are illustrated in the accoupanying figures:

A) General Corrosion

Sample DEA325: Edge of Trough Pattern The troughs are formed from corrosion in the electrolyte. The base metal protected by the photoresist during polarization is undisturbed.5

Sample DEA325: Grating left after corrosion has etched troughs. The trough depths are on the order of 135nm. 6

Line Profile Through Image DEA325.f11, showing the depths of the etched troughs..... 7

B) Local Corrosion

Localized attack was observed only at specific triple junctions, with the grain boundaries identified by optical microscopy.

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Discussion

An AFM-based measurement shows easily and unambiguously the quantity of material dissolved under the polarization conditions described above. We believe that it is a viable method for measuring general corrosion rates for short-term laboratory tests on Corrosion-Resistant Materials.

Evidence of localized corrosion was sparse. Some localized attack was observed, and because the grain boundaries of the corroded material appeared clearly in optical micrographs, the sites of localized attack which we detected could be identified as triple junctions. We emphasize that most triple junctions are not attacked, and at this time we are unable to correlate the presence or absence of triple junction attack with the specific misorientations of the associated grain boundaries. Perhaps Orientation Imaging Microscopy (OIM) cold shed light on this issue in the future.

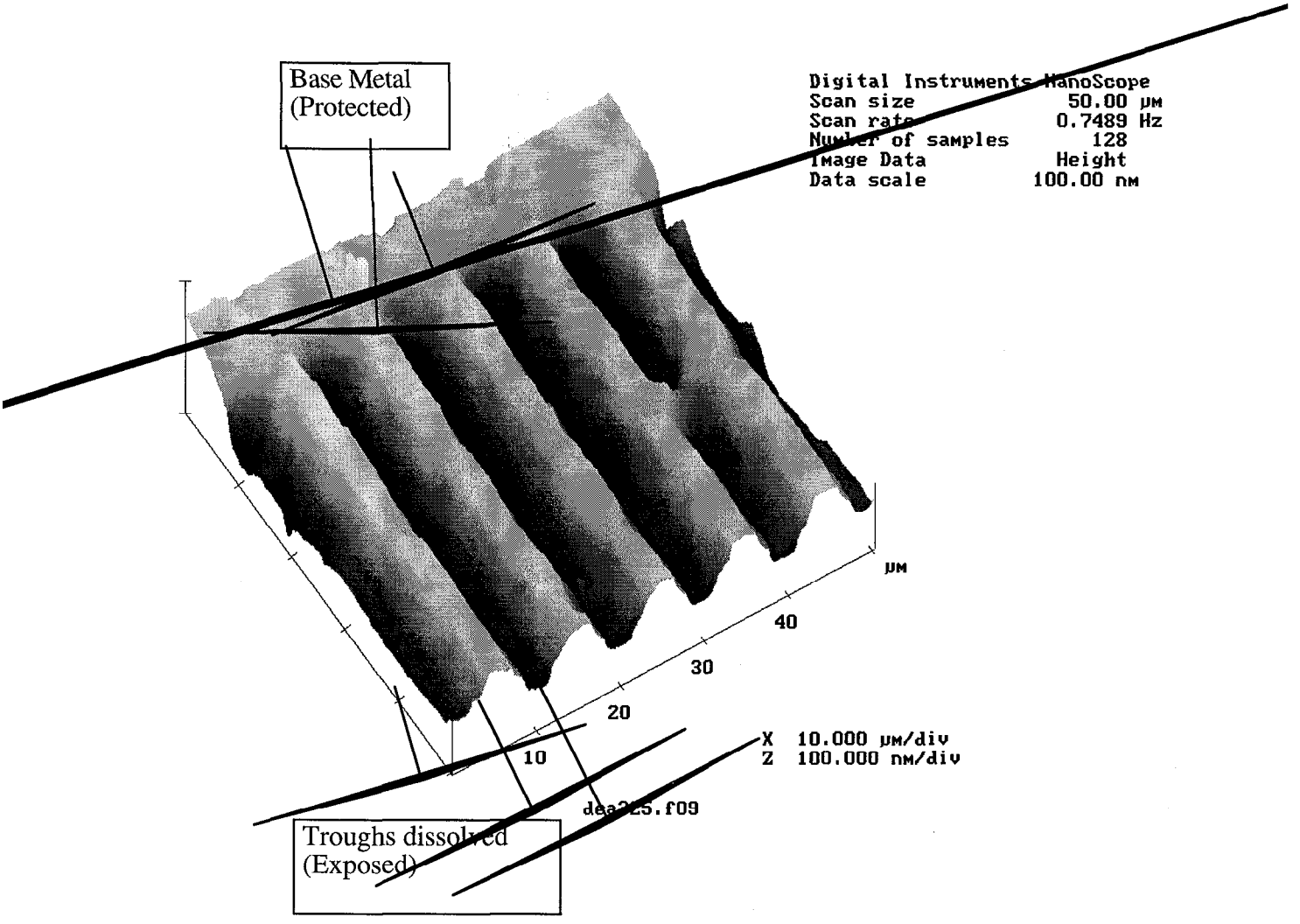
We note that a loss of 100nm of C22 on a conventional 5/8"-diameter weight loss coupon held in a holder with a gasket ID of 11mm uncompressed and 10mm compressed would represent a volume loss of 7.8×10^{-6} cm^3. Using the specific gravity of 8.69 in the

Haynes data sheet for its Hastelloy C-22, the total weight loss would be 67 μg. If the corrosion rate were, hypothetically, linear, then the total weight loss after one hour would be only 5.5μg.

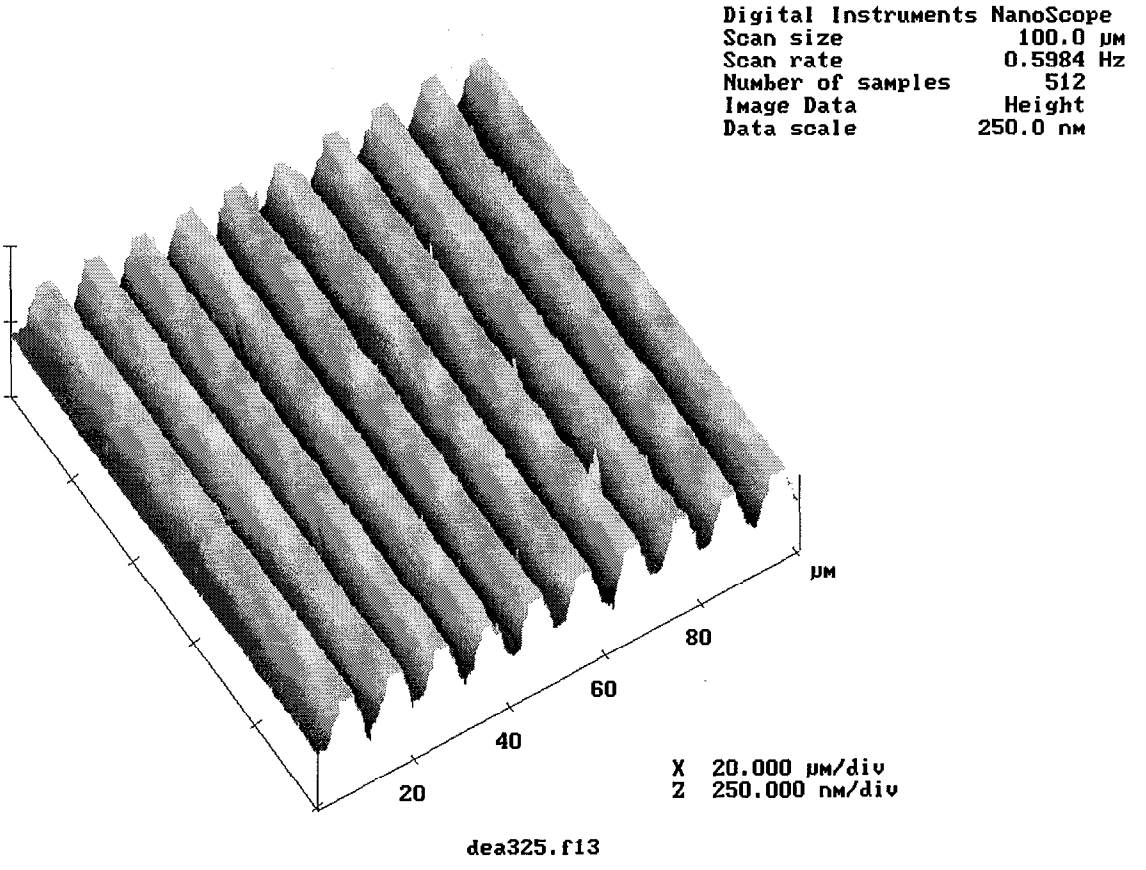
Finally, we emphasize that the one measurement presented here should not be extrapolated to a corrosion rate, because at this time we have no basis for extracting a general corrosion rate from only one data point. Many more data points will be required before we can do that.

Acknowledgments

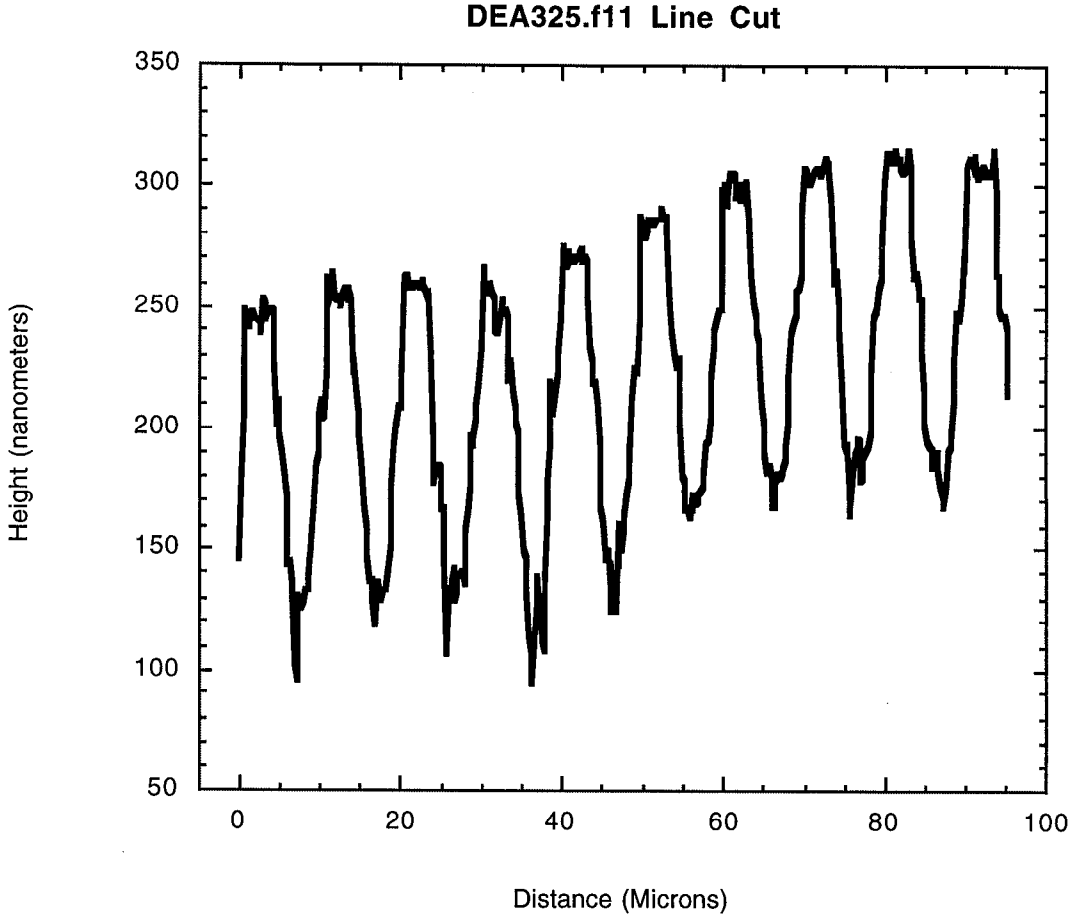
The authors are grateful to R. Kershaw for sample polishing, to D. Ciarlo for lithographic patterning, to J. Estill, K, King, S. Gordon, and L. Logoteta for electrochemical testing, and to D. Fix for assistance with AFM measurements. This work was performed at Lawrence Livermore National Laboratory under the auspices of the US Dept. of Energy under Contract W-7405-Eng-48 and was supported by the Yucca Mountain Program.



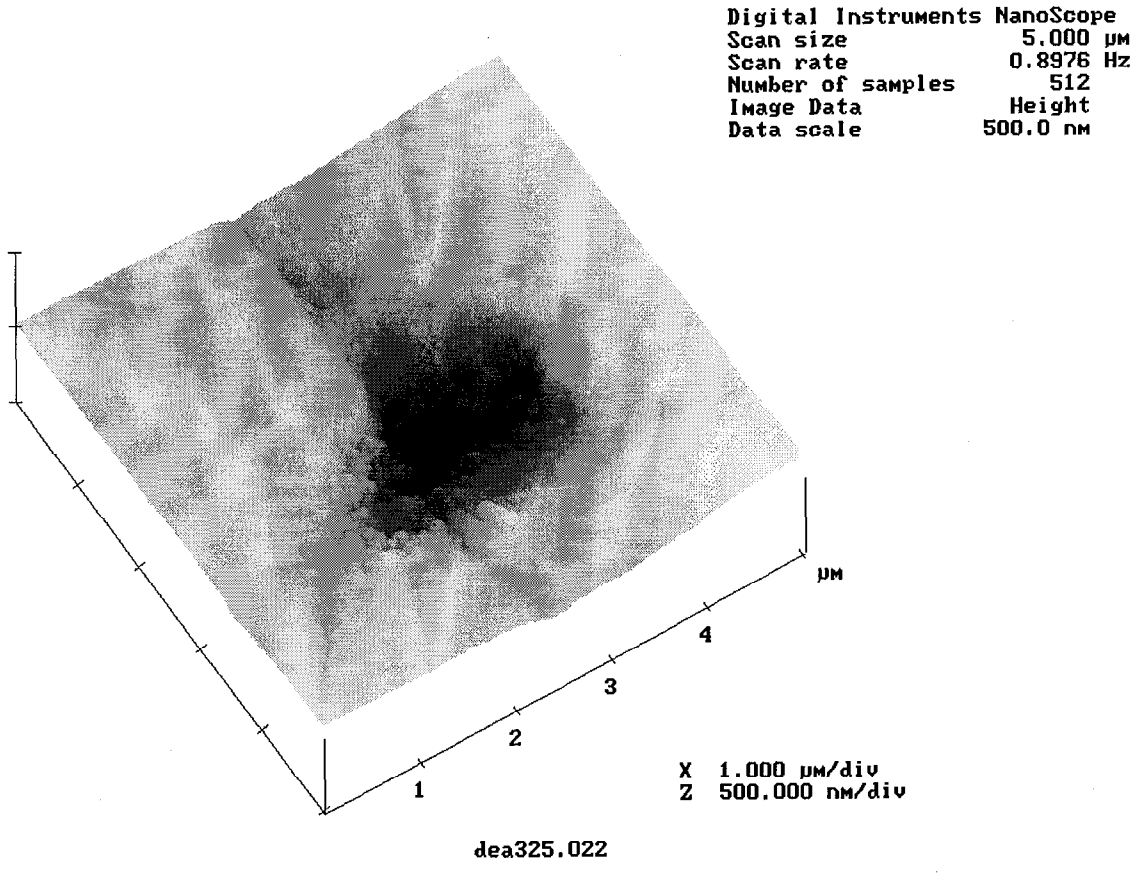
Sample DEA325: Edge of Trough Pattern The troughs are formed from corrosion in the electrolyte. The base metal protected by the photoresist during polarization is undisturbed.



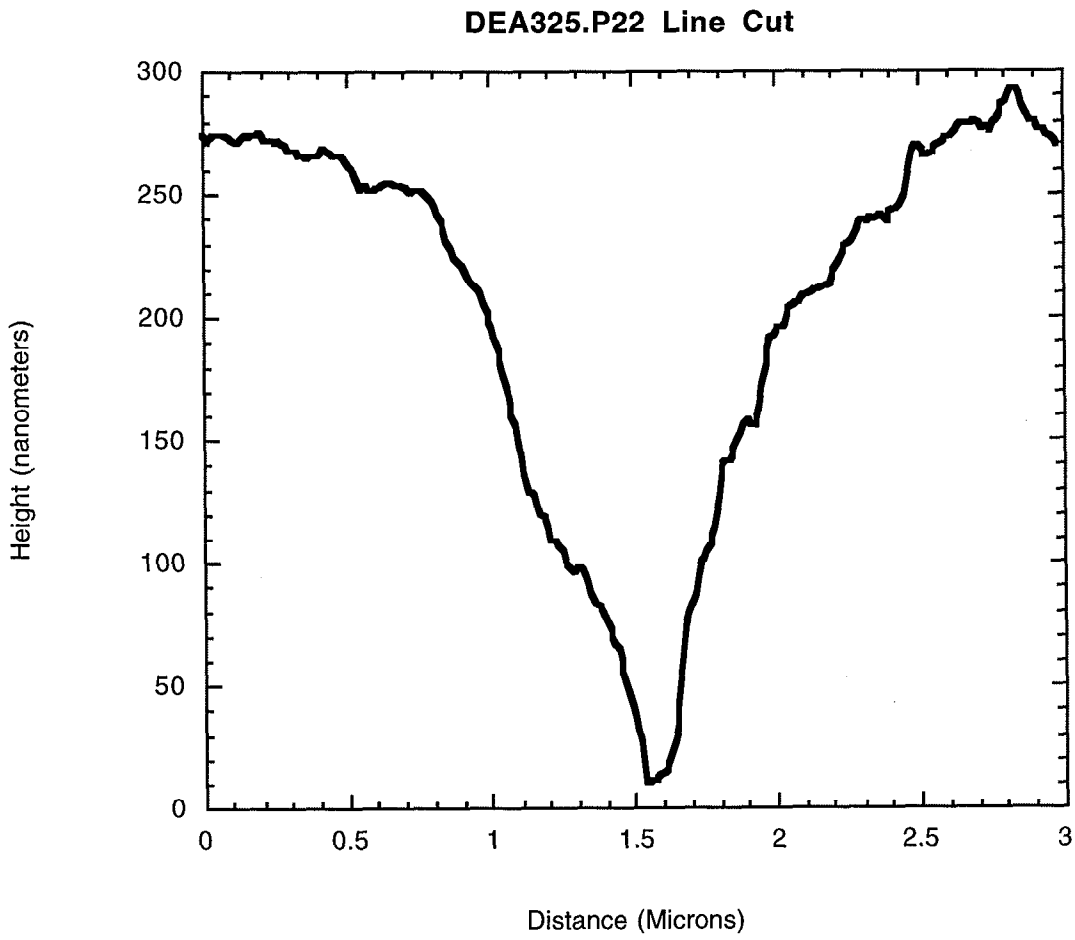
Sample DEA325: Grating left after corrosion has etched troughs. The trough depths are on the order of 135nm.



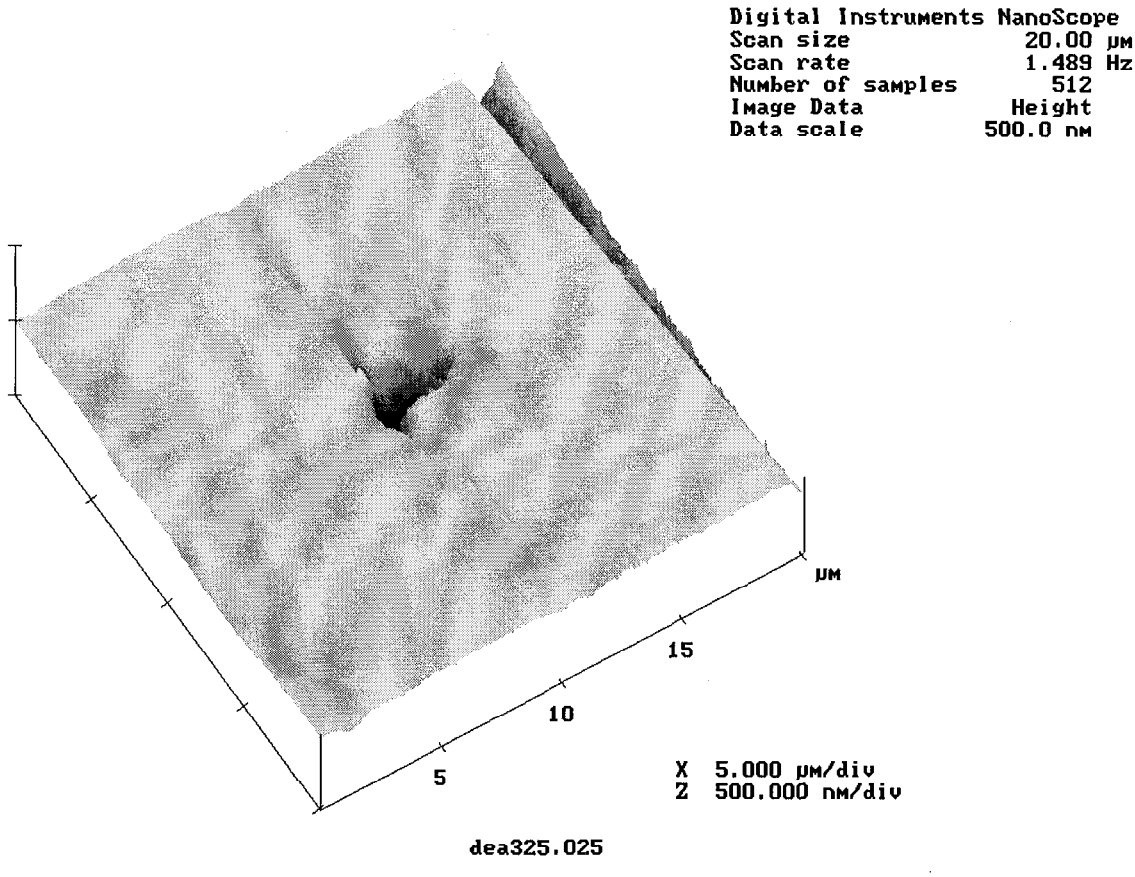
Line Profile Through Image DEA325.f11, showing the depths of the etched troughs.



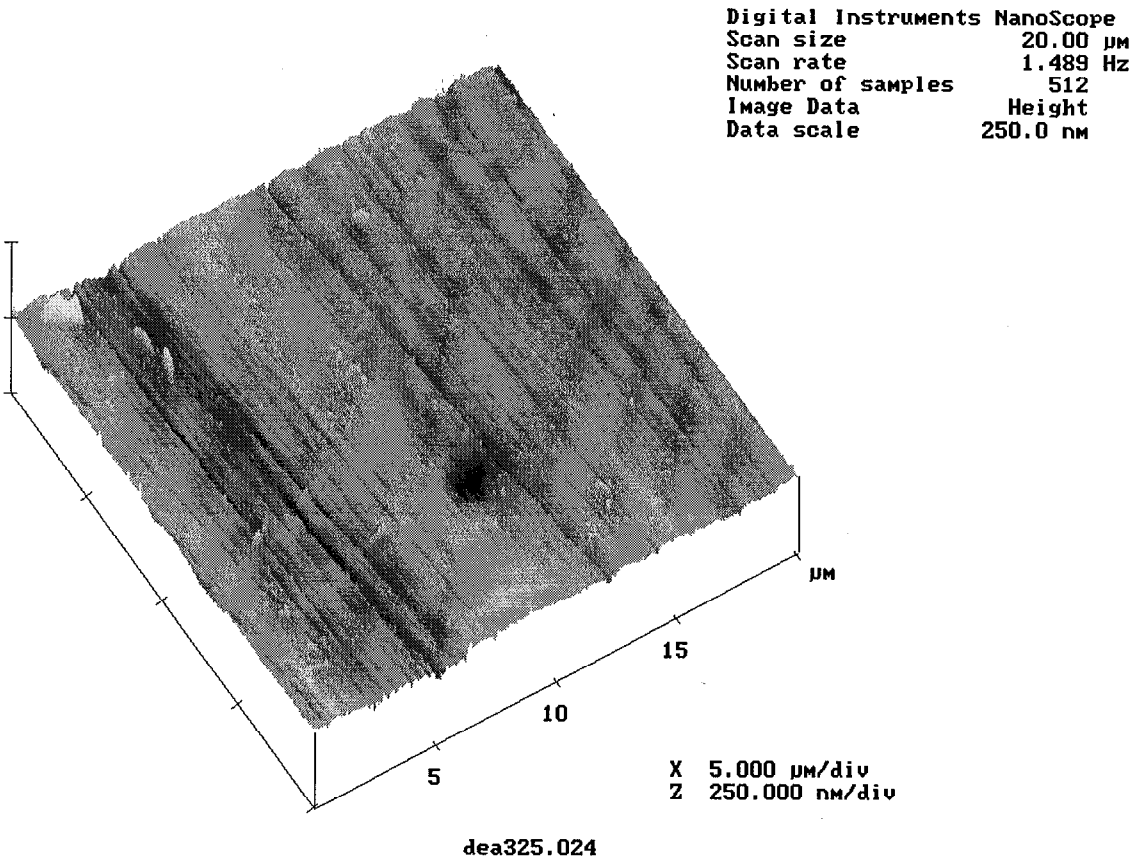
DEA325: Localized Attack at a Triple Junction



Line Cut Through the Site of Attack in Image DEA325.p22, showing a depth of 270nm.



DEA325: Localized Attack at Another Triple Junction



DEA325: Localized Attack at Yet Another Triple Junction